

It is not improbable that ethylic and methylic sulphides, &c., when treated with concentrated sulphuric acid, would form corresponding compounds.

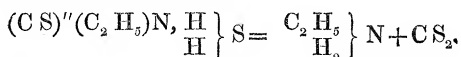
I cannot conclude this paper without acknowledging the very efficient aid I have received from my assistant, Mr. Charles E. Groves, in the preceding investigation.

IV. "Compounds Isomeric with the Sulphocyanic Ethers.—II. Homologues and Analogues of Ethylic Mustard-oil." By A. W. HOFMANN, Ph.D., M.D., LL.D. Received September 11, 1868.

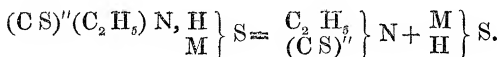
In a former Note submitted to the Royal Society some months ago*, I have sketched a series of compounds isomeric with the well-known sulphocyanic ethers; today I shall endeavour to delineate more in detail the bodies the existence of which I then pointed out.

In order to prepare these substances, which, from their analogy with the essential oil of mustard-seed, I have designated by the name of *mustard-oils*, the monamines were in the first place treated with bisulphide of carbon; the alcohol-sulphocarbonates of the monamines thus formed were then submitted to the action of heat and converted, by the loss of 1 molecule of sulphuretted hydrogen, into sulphuretted ureas, which were finally deprived of 1 molecule of monamine by means of anhydrous phosphoric acid. Circuitous as this process may appear, it has the merit of being a general one, furnishing, in fact, the mustard-oils both of the fatty and aromatic series. When working with fatty substances, however, the method may be very considerably curtailed. Let it be *ethylic mustard-oil* that is to be prepared.

Even on the threshold of my inquiry I had hoped to see ethyl-sulphocarbamic acid split up into sulphuretted hydrogen and ethylic mustard-oil; experiment, however, proved that the metamorphosis assumes another form, the acid yielding as products of decomposition its two components, ethylamine and bisulphide of carbon.



But a transformation which the free acid refuses, the metallic ethyl-sulphocarbamates undergo without difficulty, more especially in the presence of an excess of the metallic solution, a metallic sulphide being formed.



On adding, for instance, nitrate of silver to a solution of ethyl-sulphocarbamate of ethylamine, such as is produced by the action of bisulphide of carbon upon ethylamine, a white precipitate of ethyl-sulphocarbamate of silver is formed, nitrate of ethylamine passing into solution. After some time,

* Proceedings, vol. xvi. p. 254.

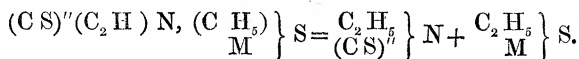
however, this precipitate blackens, even at the common temperature, more rapidly on heating, with formation of sulphide of silver. Simultaneously the odour of ethylic mustard-oil becomes perceptible; and if the liquid be heated to ebullition, this oil distils in large quantity with the vapour of water. The disengagement of sulphuretted hydrogen, which is observed at the same time, belongs to a secondary reaction, the unstable hydrosulphide of silver (which is formed in the first instance) splitting up into sulphide of silver and sulphuretted hydrogen.

In this experiment no excess of silver should be used. Ethyl mustard-oil, more especially upon protracted ebullition, exchanges its sulphur for oxygen, thus giving rise to the formation of cyanate of ethyl, easily recognizable by its fearful odour. Ultimately this ether is entirely decomposed into carbonic acid and ethylamine; after some time the solution contains nothing but nitrate of ethylamine.

Most of the metallic ethyl-sulphocarbamates, more especially the copper and mercury salts, behave exactly like the silver compound. I have almost invariably employed mercuric chloride for preparing ethyl-mustard-oil. In this case the hydrochlorate of ethylamine which is produced unites with the excess of corrosive sublimate to form an insoluble compound. Accordingly the ethylamine, which in this reaction is separated as salt, exists partly in solution, partly in the precipitate; it is easily recovered by treating with caustic soda the residue which is left after the mustard-oil has been obtained by distillation. When working with pure ethylamine, one half of the base may thus be regenerated for a new operation.

But it would be useless to employ pure ethylamine for this purpose. The crude mixture of bases, which is obtained by allowing alcoholic ammonia to stand for some time with iodide of ethyl and distilling the iodides thus formed with an alkali, is very well adapted for this operation. This mixture, as is well known, contains, together with ammonia, the primary, secondary, and tertiary monamines of the ethyl-series.

I have satisfied myself, in the first place, that diethylamine is just as easily converted into ethylic mustard-oil as ethylamine. The experiment was made with absolutely pure diethylamine prepared by means of diethyl-oxamic ether. Bisulphide of carbon, more especially in alcoholic solution, acts with great energy upon diethylamine, diethyl-sulphocarbamate of diethylamine being formed, which, when treated by a metallic salt, furnishes a metallic diethyl-sulphocarbamate together with a salt of diethylamine. On ebullition, the former is converted into ethylic mustard-oil; but instead of the metallic hydrosulphide generated in the analogous metamorphosis of ethylamine, in this case a mercaptide is formed.



I should not leave unmentioned, however, that the formation of mercaptide is still to be further proved by direct experiment. On working with

mercuric chloride, the precipitate which remains after the ethylic mustard-oil is separated by distillation, neither dissolves in boiling water nor in boiling alcohol. If this precipitate were pure mercaptide of mercury, it should be crystallizable from boiling alcohol. Probably it is a double compound of mercaptide and chloride; at all events, I have established by experiment that mercaptide and chloride of mercury unite to form a compound perfectly insoluble both in water and alcohol, even on boiling.

Triethylamine also unites with bisulphide of carbon; but this compound, as might have been expected, yields no longer any mustard-oil.

Ultimately, as regards the ammonia, which invariably occurs in the crude mixture of the ethyl-bases, its presence rather increases than diminishes the quantity of mustard-oil which is formed. This ammonia remains in the residue in the form of a salt, together with salts of ethylamine, diethylamine, and triethylamine; and a corresponding quantity of the primary and secondary ethyl-bases is converted into mustard-oil, the yield of which may thus be very considerably augmented.

The mercuric salts also attack ethylic mustard-oil, although much less easily and rapidly than nitrate of silver. A large excess of chloride of mercury, however, should be avoided. If the ethylamine be prepared from iodide of ethyl, it is convenient to employ the mercury salt and the mixture of bases in such proportions that 1 molecule of mercuric chloride reacts upon the bases generated by means of 2 molecules of iodide of ethyl.

In an experiment carried out upon rather a large scale a quantity of ethylic mustard-oil was obtained amounting to from 60 to 70 per cent. of the theoretical proportion which might have been expected from the weight of iodide of ethyl employed.

Ethylic Mustard-oil.

As to the physical properties of ethylic mustard-oil, I have not to add anything to what I have formerly stated, except a determination of the gas-volume weight, which was taken in the vacuum of the barometer at the temperature of 185° (in the vapour of boiling aniline).

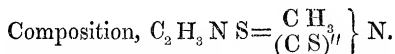
	Referred to hydrogen.		Referred to air.	
	Theory.	Experiment.	Theory.	Experiment.
Gas-volume weight	43·5	43·75	3·02	3·03

When operating with the isomeric sulphocyanide of ethyl, the following numbers were obtained :—

	Referred to hydrogen.		Referred to air.	
	Theory.	Experiment.	Theory.	Experiment.
Gas-volume weight of sulphocyanide of ethyl (determined in the vapour of boiling water)	43·5	42·84	3·02	2·98

Methylic Mustard-oil.

I formerly obtained the methyl-compound as an oily liquid boiling at 120°, and powerfully smelling of horseradish. When a somewhat larger quantity of this body was prepared according to the process above described, the liquid, after distillation with the vapour of water, solidified to a splendid crystalline body.

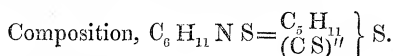


Boiling-point 119°; fusing-point 34°; solidifying-point 26°.

	Referred to hydrogen.		Referred to air.	
	Theory.	Experiment.	Theory.	Experiment.
Gas-volume weight of methylic mustard-oil (determined in the vapour of boiling water)	36·5	37·89	2·52	2·61

Amylic Mustard-oil.

I have also prepared the amyl-compound on a larger scale by a slight modification of the process above described. Instead of separating the compound from the mercury precipitate obtained in the dilute alcoholic solution at once by distillation, it is advisable to return the vapours, condensed by a cooler, for some time to the boiling mixture. When the reaction is complete, the sulphide of mercury is filtered off, the amylic mustard-oil precipitated by water, dried over chloride of calcium, and ultimately purified by distillation. The odour of the compound is analogous to those of the methyl- and ethyl-body, but less pronounced.



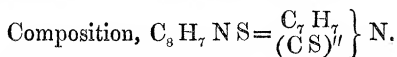
Boiling-point 183° to 184°.

	Referred to hydrogen.		Referred to air.	
	Theory.	Experiment.	Theory.	Experiment.
Gas-volume weight of amylic mustard-oil (determined in the vapour of boiling aniline)	64·5	63·42	4·48	4·40

Tolylic Mustard-oil.

As has already been pointed out, the new process cannot be used for preparing the mustard-oils of the aromatic series, at all events in the narrower sense of the word. I may mention, however, that tolylic mustard-oil may be readily obtained by the process which I had formerly used for producing the corresponding compound of the phenyl-series. The ditolylsulphocarbamide required for this purpose is known; it was examined some years ago by M. Sell. If this body be distilled with anhydrous phosphoric acid, aromatic vapours are evolved which may be condensed to a yellowish oil rapidly assuming the crystalline form. The product of distillation

generally retains a minute quantity of ditolyl-sulphocarbamide, which may be separated by recrystallization from ether, tolylic mustard-oil being extremely, ditolyl-sulphocarbamide but slightly soluble in this liquid. The mustard-oil of the tolyl-series readily crystallizes in beautiful white needles, attaining often the length of several centimetres; they are easily soluble in alcohol, slightly so in water. Tolylic mustard-oil possesses to an almost deceptive degree the odour of oil of aniseed.



Boiling-point 237° ; fusing-point 26° ; solidifying-point 22° .

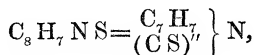
When gently heated with toluidine, tolylic mustard-oil is reconverted into ditolylsulphocarbamide. With ammonia it forms sulphuretted monotolyl-urea. Aniline gives rise to the mixed sulphuretted urea of the phenyl and tolyl-series, which is easily obtained in beautiful crystals.

Benzylc Mustard-oil.

Chemists are acquainted with a primary monamine isomeric with toluidine. This is benzylamine, discovered by M. Mendius. Since the beautiful experiments of MM. Fittig and Tollens have established the presence of the methyl-group in toluol, our views respecting the difference of constitution of the two isomeric monamines have acquired a solid foundation. In toluidine the substitution of the primary ammonia fragment ($H_2 N$) for hydrogen has taken place within the benzol nucleus; in benzylamine, on the other hand, the substitution occurs in the methyl-group engrafted upon the benzol nucleus. Benzylamine thus belongs, in a measure, to both the fatty and the aromatic series; and the residue of ammonia, which in fact is exclusively affected during the formation of mustard-oils, is present in the fatty portion of the compound. Under these circumstances it appeared rather probable that the base isomeric with toluidine would yield its mustard-oil by conversion into the bisulphide-of-carbon compound and distillation of the latter with perchloride of mercury. Experiment has verified this anticipation.

Benzylamine dissolves in bisulphide of carbon with evolution of heat, a beautiful white crystalline compound being formed, which, when distilled with alcohol and mercuric chloride, yields a liquid of a penetrating odour. On adding water to the alcoholic distillate, the mustard-oil separates in clear drops which are heavier than water.

Benzylc mustard-oil,



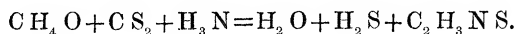
isomeric with tolylic mustard-oil, boils at about 243° , a few degrees higher than the tolyl-compound. The new body possesses in an eminent degree the odour of water-cresses. The resemblance is so striking, that it becomes desirable to examine the essential oil of water-cresses.

I may here mention that menaphtylamine, the preparation and pro-

perties of which I have lately described to the Royal Society*, yields likewise a mustard-oil, if it be successively treated with bisulphide of carbon and mercuric chloride. I have not, however, more minutely examined this compound.

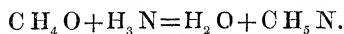
All the mustard-oils here mentioned exhibit, more especially with reference to ammonia and its derivatives, the same reactive power which belongs to ethylic mustard-oil, more minutely described in my former communication, and by which the mustard-oil *par excellence*, the well-known allyl-compound, has long fixed the interest of chemists. Of the legion of urea-like bodies which are here possible, I have prepared but few. It may be stated that the sulphuretted methylic and amylic ureas, and also the sulphuretted methylamylic and amyltolylic ureas vie with each other as to beauty and facility of crystallization. I have not, however, examined more minutely these ammonia compounds, their study promising but very little scientific gain. On the other hand, I have investigated with some care the metamorphoses of the mustard-oils, since their comparison with the corresponding transformations of the sulphocyanic ethers promised to elucidate the different construction of the two groups of bodies.

The results of these inquiries unequivocally confirm the view suggested by the formation of the two classes of compounds. It is indeed only necessary to trace their origin in order to understand the nature of this difference. We could not select better illustrations than the isomeric terms of the methyl-series. Both bodies, methylic mustard-oil and sulphocyanide of methyl, are in the last instance derived from exactly the same compounds, viz. methylic alcohol, bisulphide of carbon, and ammonia. Let the molecules of these three compounds unite with separation of 1 molecule of water and 1 molecule of sulphuretted hydrogen, and a body will be formed possessing the composition of both methylic mustard-oil and sulphocyanide of methyl.

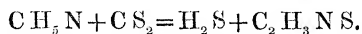


Accordingly the nature of the body produced must depend upon the conditions (it might be almost said upon the order) in which the molecules of water and sulphuretted hydrogen are separated from the aggregate of atoms.

Conceived in its simplest form, the first step of the generation of methylic mustard-oil consists in the action of ammonia upon methylic alcohol, when methylamine is produced with separation of water.

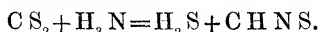


In a second phase of the process, methylamine is acted upon by bisulphide of carbon, the products being methylic mustard-oil and sulphuretted hydrogen.

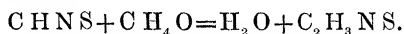


* Proceedings, vol. xvi. p. 445.

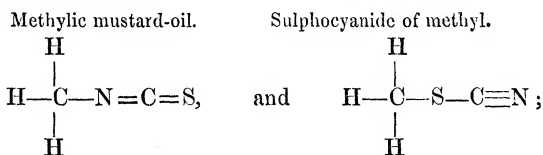
The reactions occur in the inverse order when sulphocyanide of methyl is produced. Here the process commences with the reaction between bisulphide of carbon and ammonia, hydrosulphocyanic acid being formed with separation of sulphuretted hydrogen.



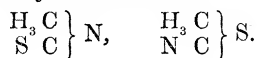
Hydrosulphocyanic acid and methylic alcohol, lastly, furnish water and sulphocyanide of methyl.



This inverse order, in which the reactions succeed each other, gives a definite direction to our speculations as to the arrangement of the atoms within the molecules of the two compounds. If bisulphide of carbon, SCS , in contact with methylamine, $\text{H}_3 \text{CNH}_2$, is found to disengage sulphuretted hydrogen, we cannot doubt that the carbon-atom of the bisulphide, meeting, as it were, with its two freed attraction-units those liberated in the nitrogen atom, associates with this nitrogen-atom, and consequently that it must be by the nitrogen that the carbon of the methyl-group is chained to the carbon of the bisulphide. On the other hand, if in hydrosulphocyanic acid we may conceive the hydrogen to be in union with the sulphur, we are, after this hydrogen has been converted into water by the hydroxyl of methylic alcohol, also justified in considering the sulphur-atom as the link of connexion between the two carbon-atoms of the compound, the attraction-unit, which has become available in the carbon-atom, being saturated by the free atomic power of the sulphur. The relative position of the atoms in the molecules of the two compounds would thus be indicated by the following diagram—



or more concisely in the subjoined formulæ—



If this conception be correct, it is obvious that whenever nitrogen and sulphur are found together in a molecule, this molecule must be capable of existing in two different forms, one corresponding to methylic mustard-oil, the other to cyanide of methyl.

In a paper which I hope shortly to submit to the Royal Society, I propose to show how far this conception is supported by experiment.